

Química Inorgânica II

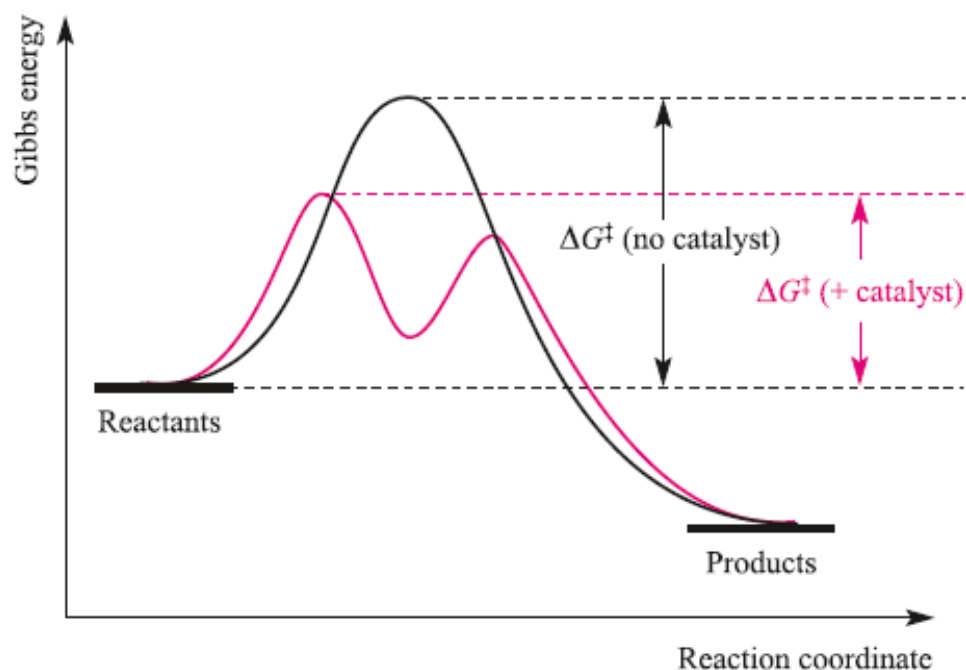
Prof. Sofia Nikolaou

TÓPICOS EM QUÍMICA DE COORDENAÇÃO

Catálise Inorgânica

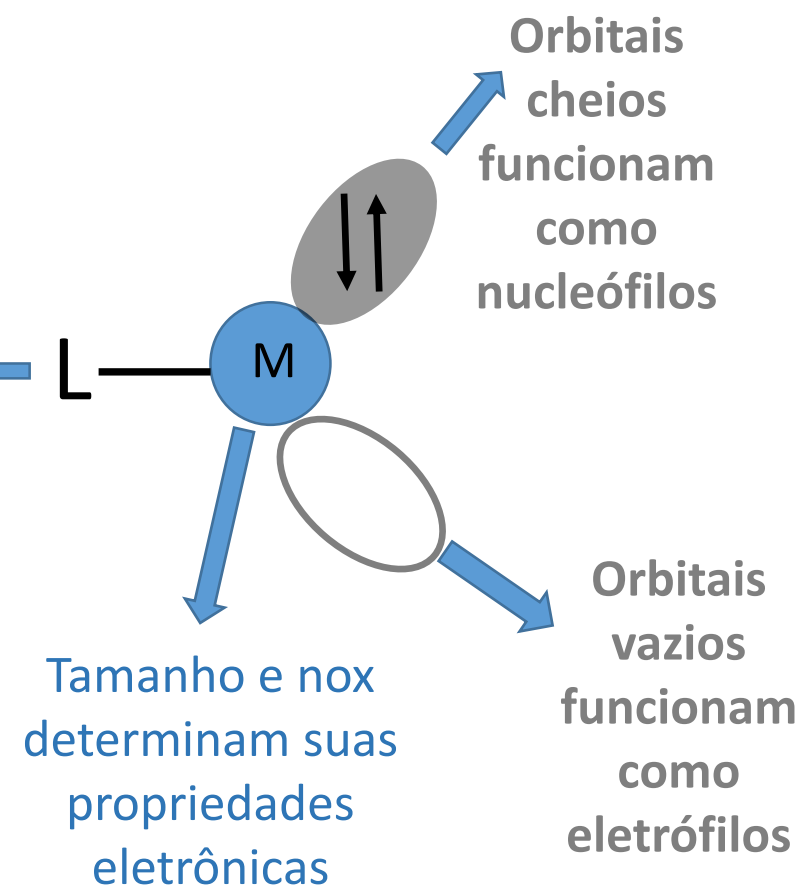
CATALISADOR

* Espécie química que não é nem um reagente, nem um produto de uma reação, mas que ALTERA o caminho através do qual a reação acontece. A alteração de caminho de reação diminui a E_a numa reação catalisada, aumentando sua velocidade em relação à reação não catalisada



- *Na perspectiva da química inorgânica, o **centro metálico** em um complexo de coordenação ou em um composto organometálico é quem **tem papel principal**.
- *O **substrato** é tratado como um **ligante**

Os ligantes modulam as propriedades eletrônicas do centro metálico e determinam suas propriedades stereoquímicas

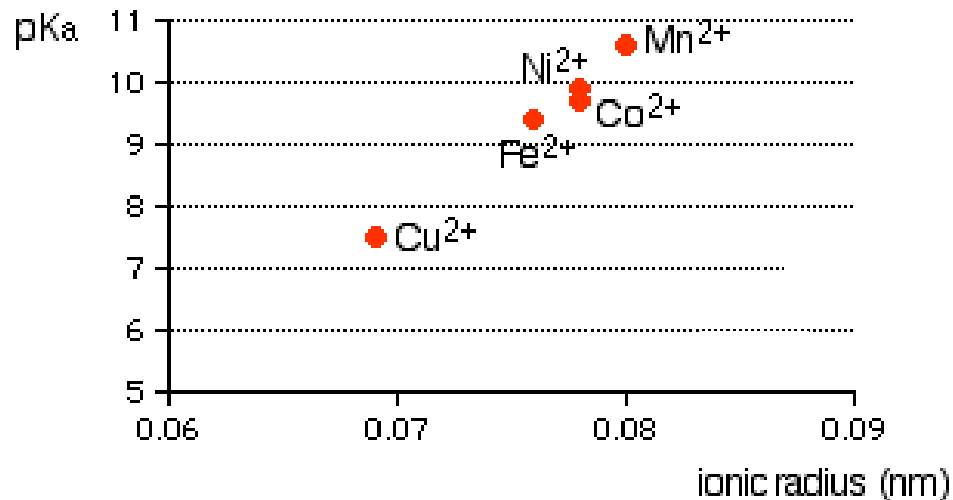


IDEIA CENTRAL

Complexos de coordenação e compostos organometálicos **ativam ligações** estáveis e oferecem **controle estereoquímico**

* **“Ativação” de ligações químicas** pela interação com um centro metálico: o caso da água

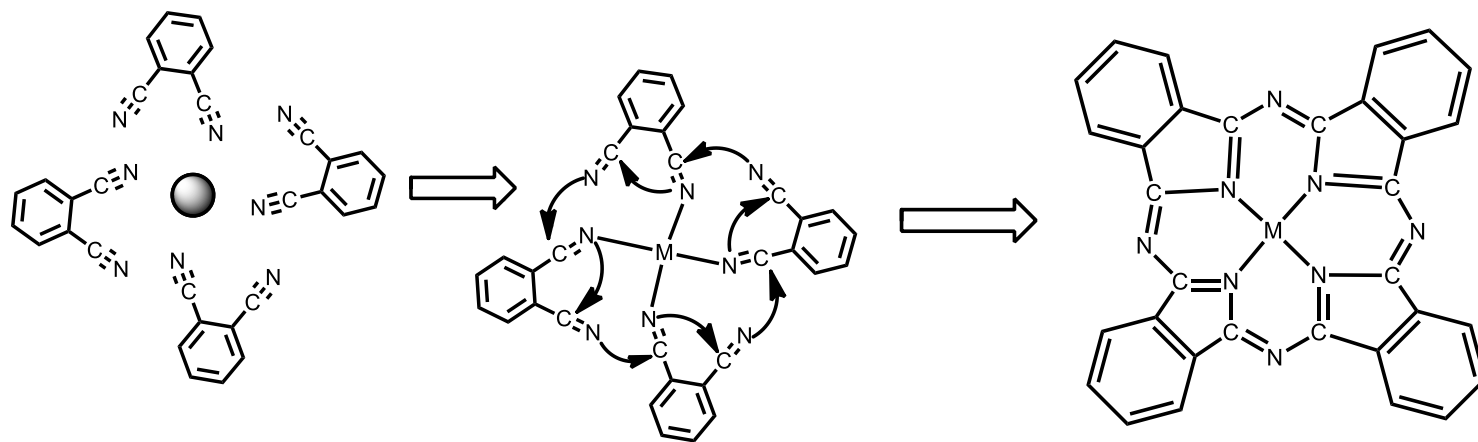
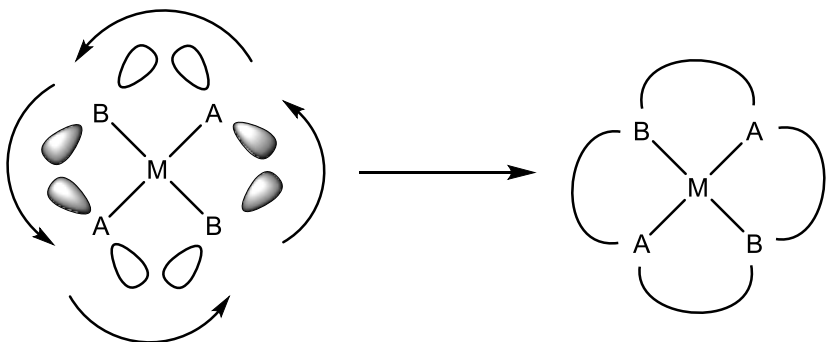
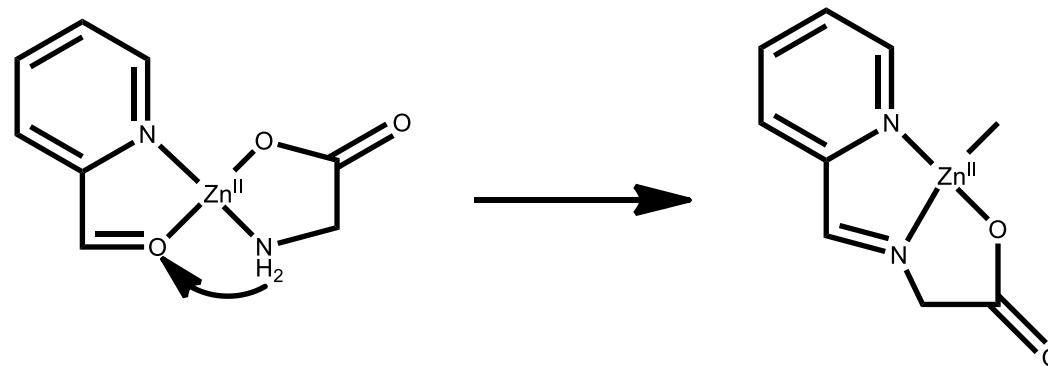
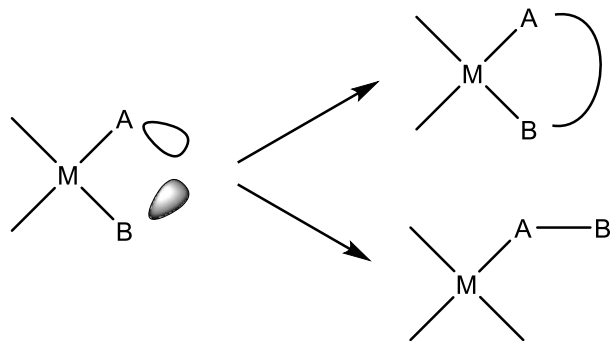
Observa-se empiricamente que, no caso de aquo-complexos, as moléculas de água coordenadas são mais ácidas do que a água livre. Nesse caso, **o centro metálico funciona como ácido de Lewis**



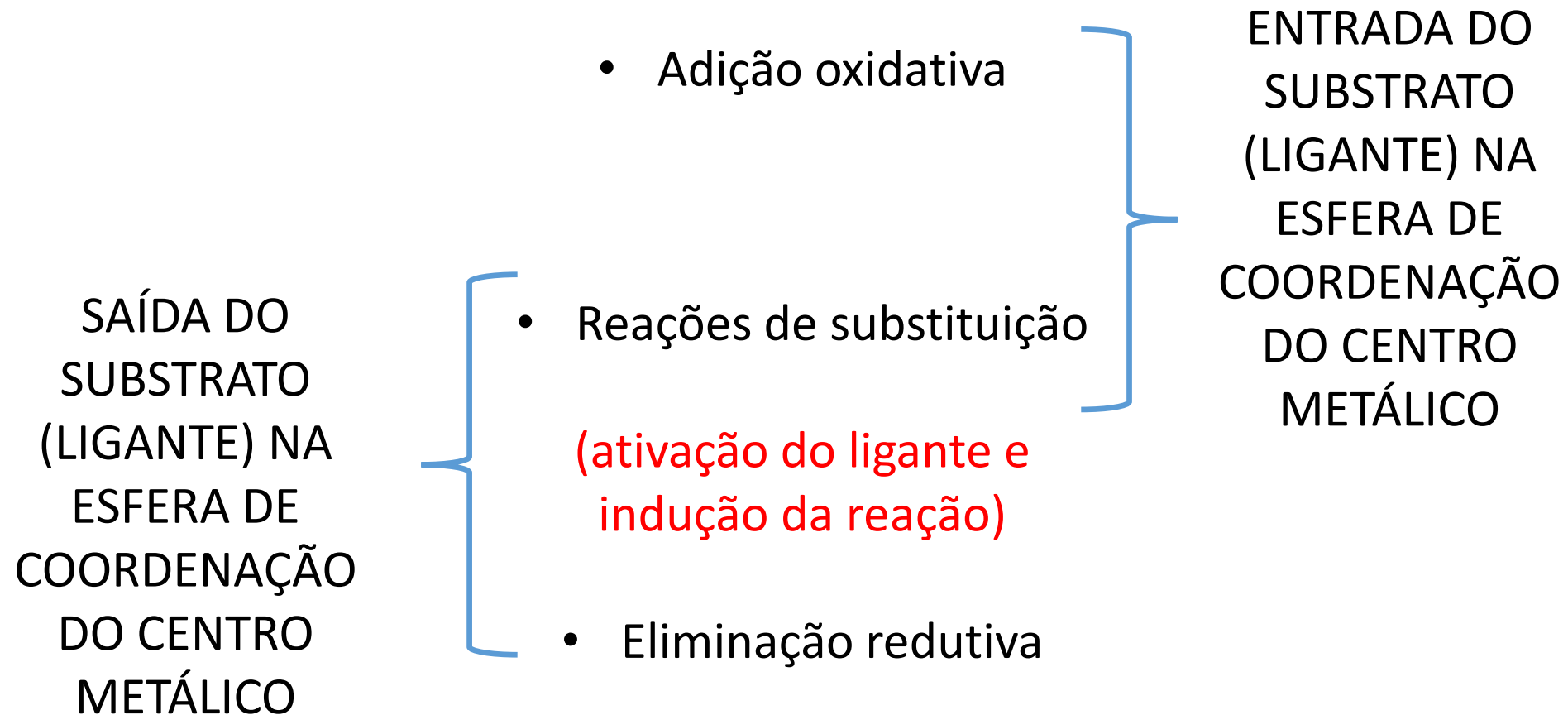
MAS...**metais podem atuar como bases de Lewis**, por retrodoação. Como é o caso dos **compostos organometálicos!!**

*controle estereoquímico

1) Efeito de organização: a aproximação entre dois ligantes, a partir da coordenação a um centro metálico, pode promover a reação entre eles. **EFEITO TEMPLATE (MOLDE)**

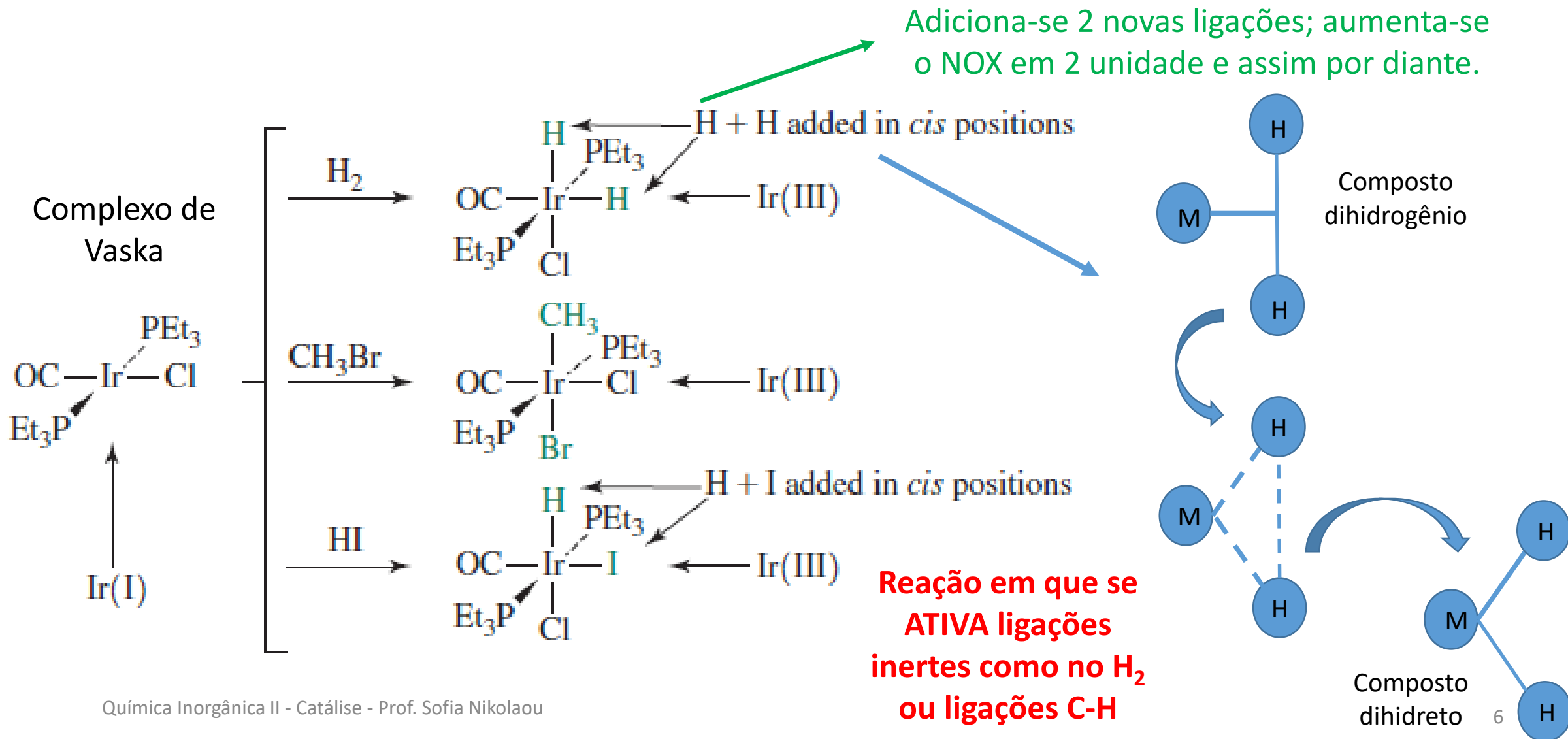


TIPOS DE REAÇÕES DE INTERESSE EM CATÁLISE



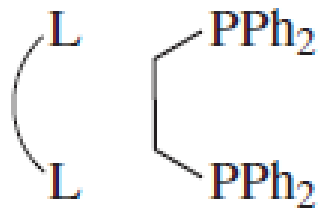
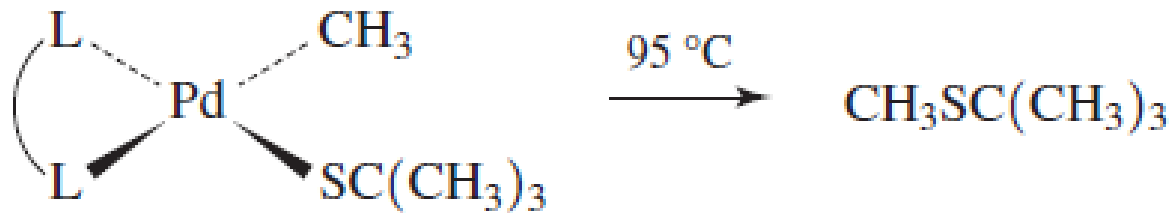
TIPOS DE REAÇÕES DE INTERESSE EM CATÁLISE – ADIÇÃO OXIDATIVA

*Oxidativa do ponto de vista do metal; é típica em complexos originalmente com número de coordenação baixo, ocorre com **aumento no NC** e consequente **aumento no NOX** do centro metálico

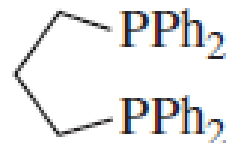


TIPOS DE REAÇÕES DE INTERESSE EM CATÁLISE – ELIMINAÇÃO REDUTIVA

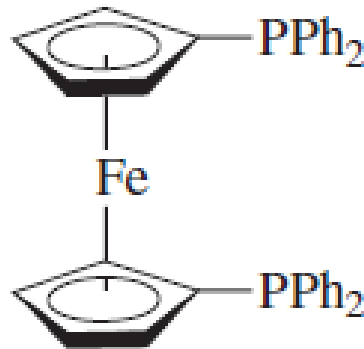
*inverso da adição oxidativa. Ao contrário da reação anterior, onde se ativa uma ligação (no sentido de enfraquecê-la e quebrá-la), a **eliminação redutiva** serve para **formar ligações** H-H, C-H, C-C, C-X, etc.



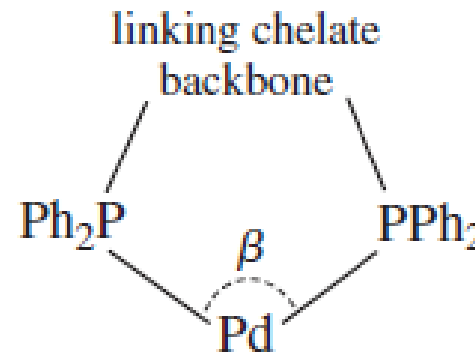
DPPE



DPPP



DPPF



Bite angle = β

A depender do ângulo de cone da fosfina e do impedimento estérico causado por ela, facilita-se a formação da ligação S-C

Ciclo catalítico

- A partir desse repertório de reações e efeito template, os compostos com centros metálicos são capazes de assistir um enorme número de reações
- Ortometalação de moléculas orgânicas
- Transmetalração
- Acoplamento cruzado
- Ativação e quebra de ligações C-C; C-H, etc.
- Hidrogenação de ligações múltiplas
- Metátese (quebra e formação de ligações C-H SEM mudança de oxidação do centro metálico)
- ROMP (“ring-opening metathesis polymerization”)
- polimerização, etc, etc.



VAMOS DESCREVER *ALGUNS*
EXEMPLOS USADOS
INDUSTRIALMENTE

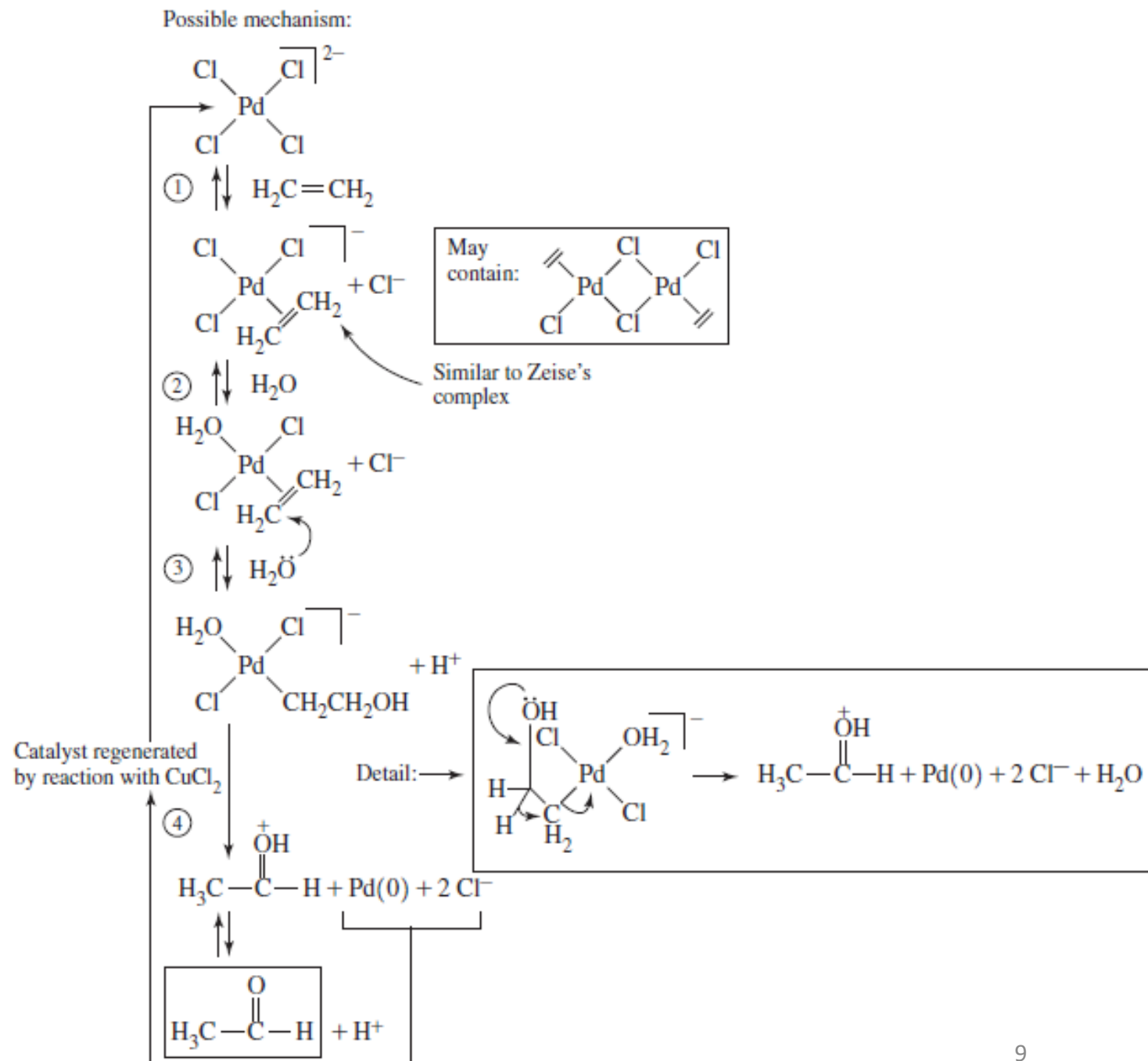
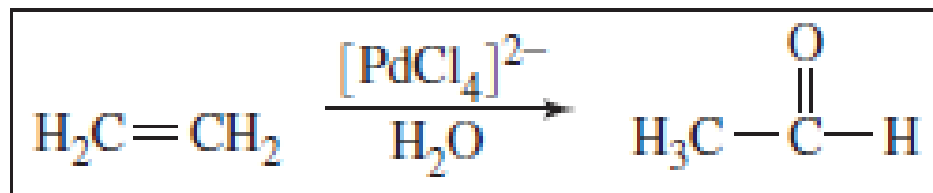
*ciclo catalítico: sequência de reações estequiométricas, normalmente reversíveis, que formam um *loop*. O catalisador precisa ser regenerado, para participar do loop novamente

*catálise homogênea: quando catalisador e reagentes estão em meio homogêneo

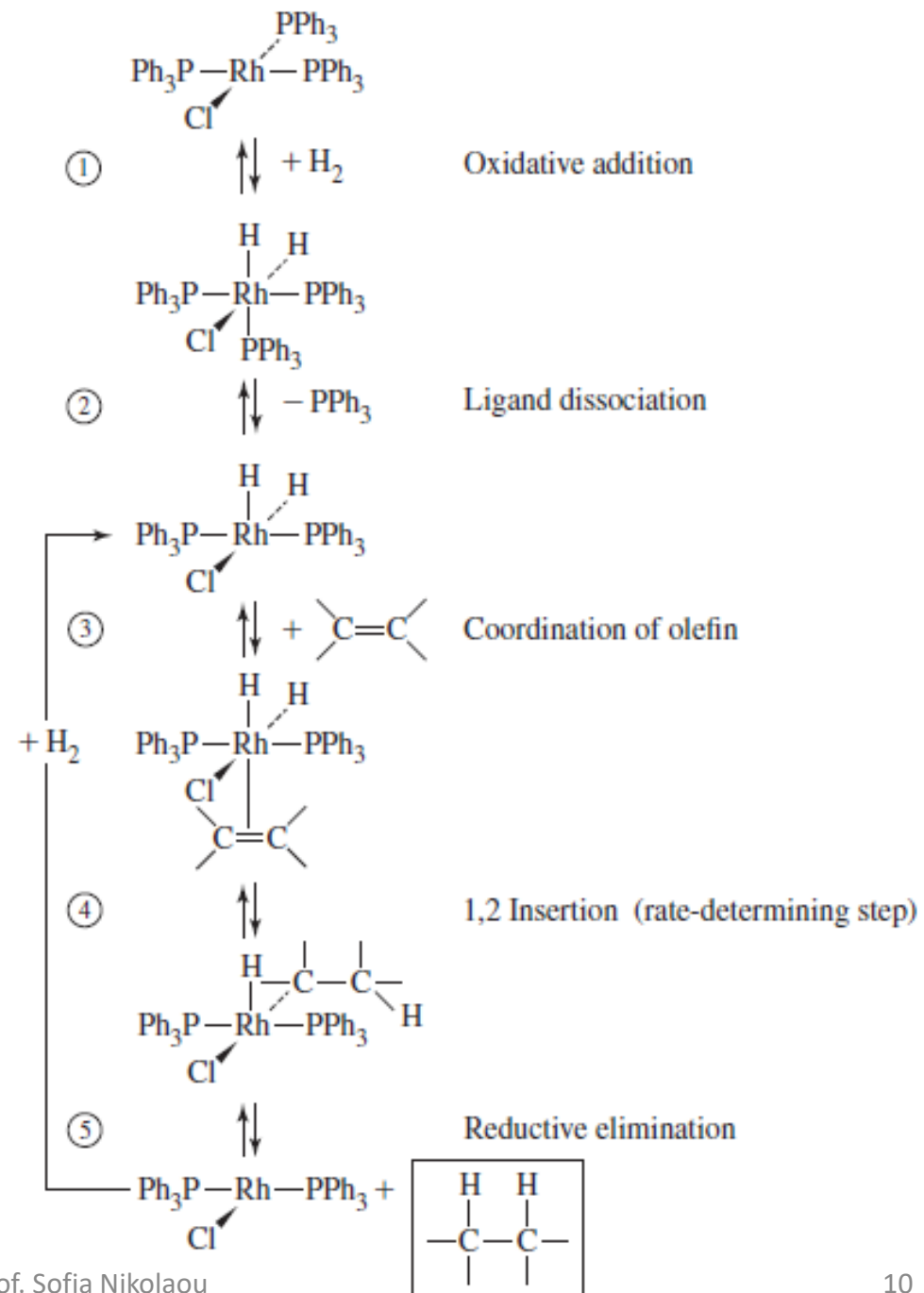
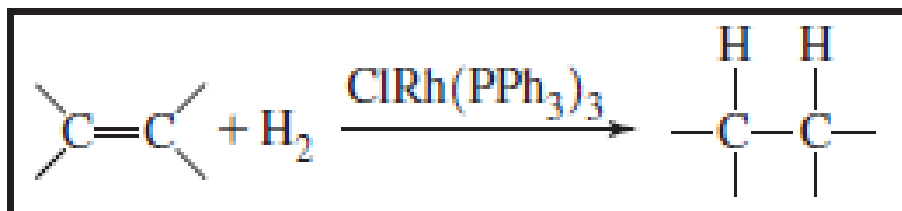
*catálise heterogênea: quando catalisador e reagentes estão em fases diferentes

PROCESSO WACKER – (1964) Síntese do acetaldeído

Acetaldeído: matéria prima do ácido acético e do acetato de etila; anualmente produz-se mais de 3 milhões de toneladas/ano de acetaldeído

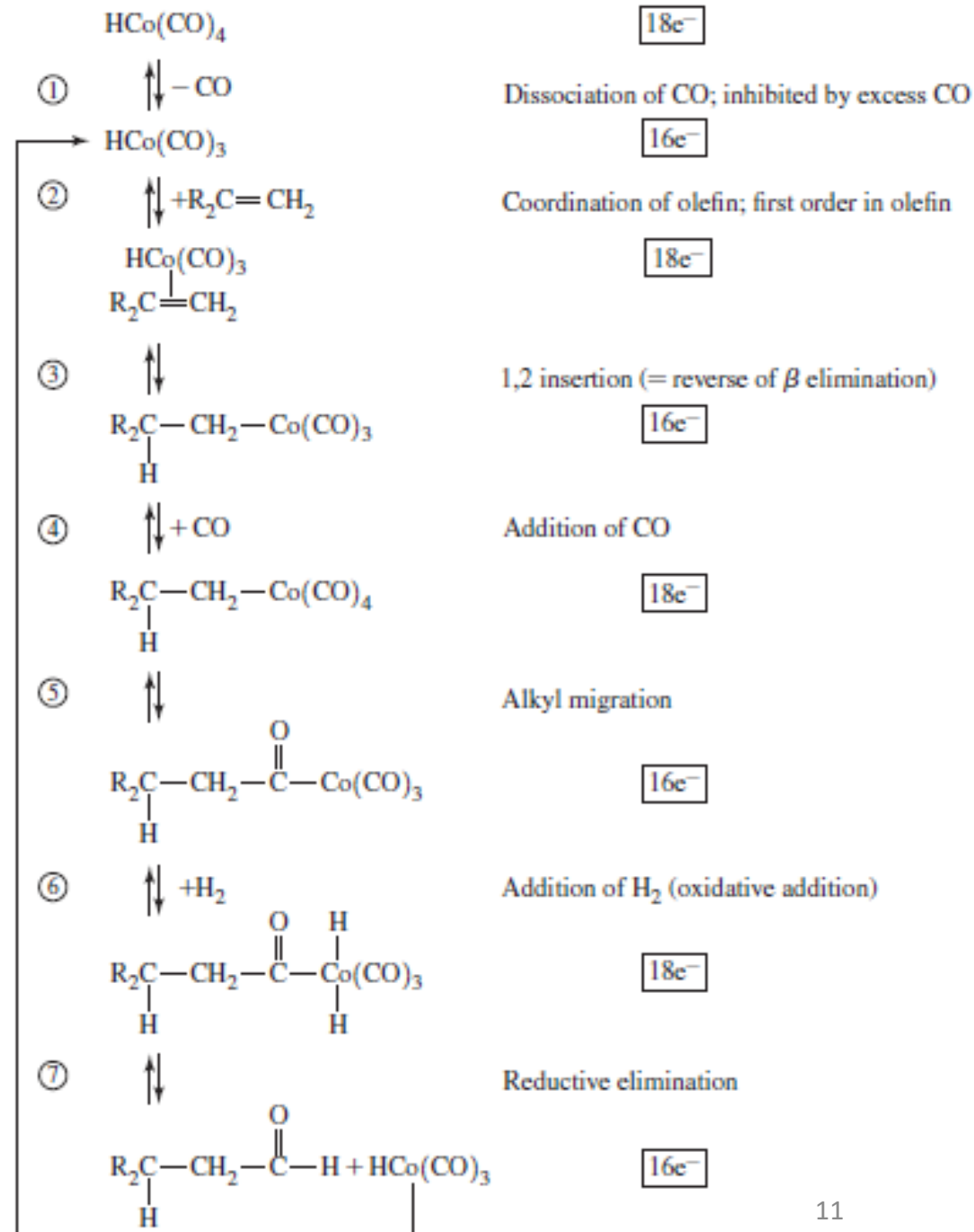
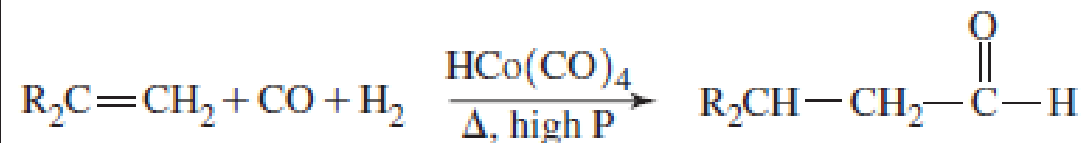


CATALISADOR DE WILKINSON– (1965) Hidrogenação catalítica



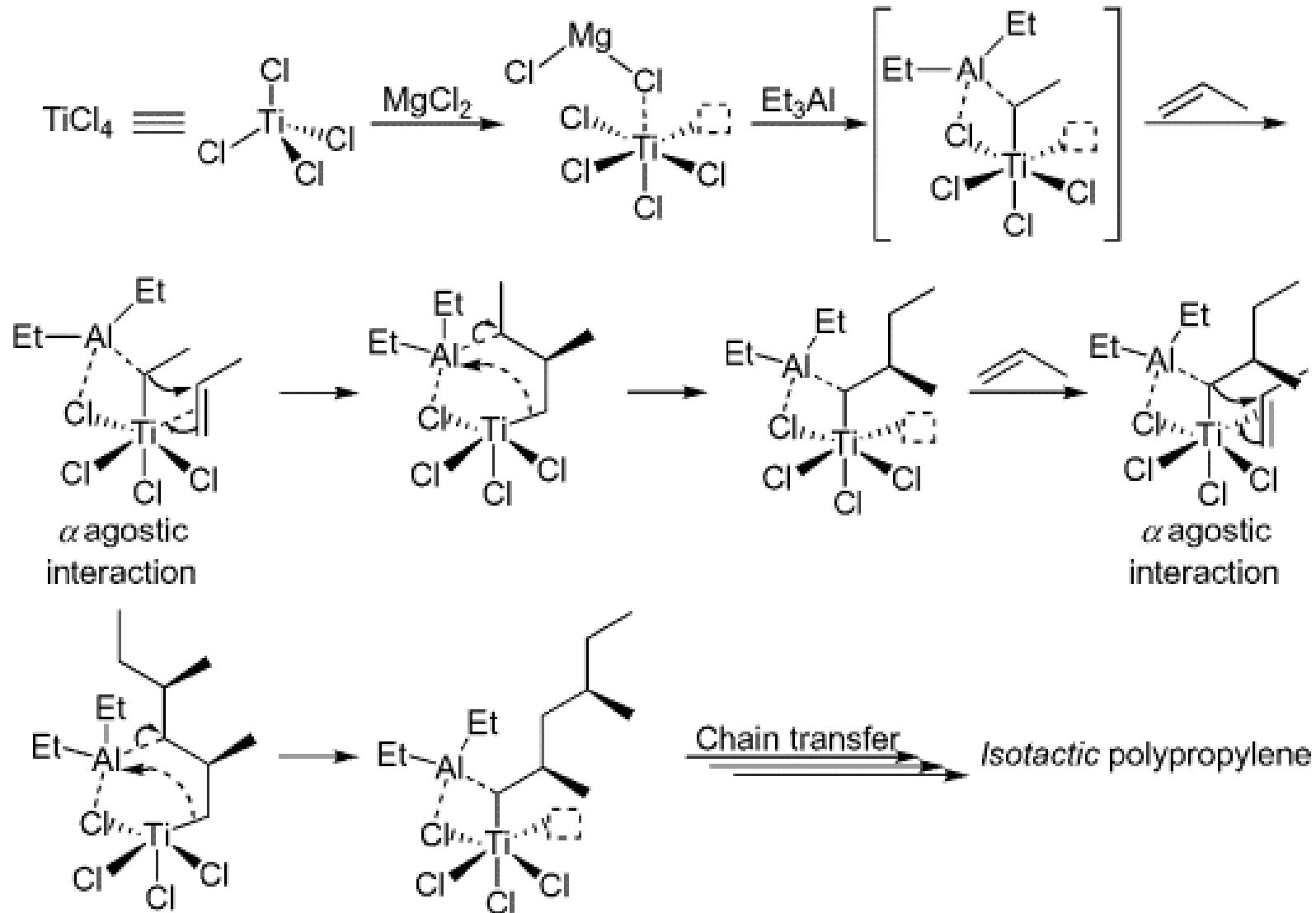
HIDROFORMILAÇÃO OU PROCESSO OXO– (1938)

Processo mais antigo de catálise homogênea utilizado industrialmente



ZIEGLER-NATTA– (1955; Nobel 1963) Polimerização de alkenos

CATALISADOR HETEROGÊNEO

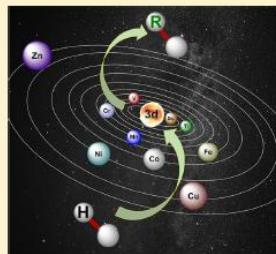


3d Transition Metals for C–H Activation

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ABSTRACT: C–H activation has surfaced as an increasingly powerful tool for molecular sciences, with notable applications to material sciences, crop protection, drug discovery, and pharmaceutical industries, among others. Despite major advances, the vast majority of these C–H functionalizations required precious 4d or 5d transition metal catalysts. Given the cost-effective and sustainable nature of earth-abundant first row transition metals, the development of less toxic, inexpensive 3d metal catalysts for C–H activation has gained considerable recent momentum as a significantly more environmentally-benign and economically-attractive alternative. Herein, we provide a comprehensive overview on first row transition metal catalysts for C–H activation until summer 2018.

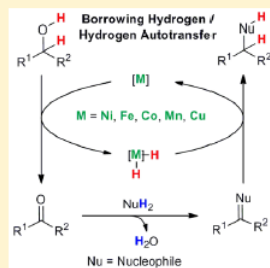


3d-Metal Catalyzed N- and C-Alkylation Reactions via Borrowing Hydrogen or Hydrogen Autotransfer

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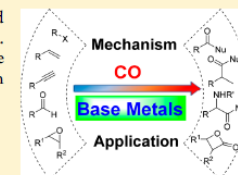
ABSTRACT: The conservation of our element resources is a fundamental challenge of mankind. The development of alcohol refunctionalization reactions is a possible fossil carbon conservation strategy since alcohols can be obtained from indigestible and abundantly available biomass. The conservation of our rare noble metals, frequently used in key technologies such as catalysis, might be feasible by replacing them with highly abundant metals. The alkylation of amines by alcohols and related C–C coupling reactions are early examples of alcohol refunctionalization reactions. These reactions follow mostly the borrowing hydrogen or hydrogen autotransfer catalysis concept, and many 3d-metal catalysts have been disclosed in recent years. In this review, we summarize the progress made in developing Cu, Ni, Co, Fe, and Mn catalysts for C–N and C–C bond formation reactions with alcohols and amines using the borrowing hydrogen or hydrogen autotransfer concept. We expect that the findings in this field will inspire others to develop new efficient and selective earth-abundant metal catalysts for borrowing hydrogen or hydrogen autotransfer applications or to develop novel alcohol refunctionalization reactions that can be mediated by such metals.

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First-Row Transition-Metal-Catalyzed Carbonylative Transformations of Carbon Electrophiles

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ABSTRACT: The main contributions in the field of first-row transition-metal-catalyzed (base-metal-catalyzed) carbonylative transformations have been summarized and discussed. The contents have been divided according to the electrophiles applied, followed by the different types of nucleophiles. Their reaction mechanisms and applications have been emphatically discussed.



Computational Approach to Molecular Catalysis by 3d Transition Metals: Challenges and Opportunities

Konstantinos D. Vogiatzis,^{*,†} Mikhail V. Polynski,[‡] Justin K. Kirkland,[†] Jacob Townsend,[†] Ali Hashemi,[§] Chong Liu,[§] and Evgeny A. Pidko^{*,‡,§}[†]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States[‡]TheoMAT group, ITMO University, Lomonosova 9, St. Petersburg 191002, Russia[§]Inorganic Systems Engineering group, Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

ABSTRACT: Computational chemistry provides a versatile toolbox for studying mechanistic details of catalytic reactions and holds promise to deliver practical strategies to enable the rational *in silico* catalyst design. The versatile reactivity and nontrivial electronic structure effects, common for systems based on 3d transition metals, introduce additional complexity that may represent a particular challenge to the standard computational strategies. In this review, we discuss the challenges and capabilities of modern electronic structure methods for studying the reaction mechanisms promoted by 3d transition metal molecular catalysts. Particular focus will be placed on the ways of addressing the multiconfigurational problem in electronic structure calculations and the role of expert bias in the practical utilization of the available methods. The development of density functionals designed to address transition metals is also discussed. Special emphasis is placed on the methods that account for solvation effects and the multicomponent nature of practical catalytic systems. This is followed by an overview of recent computational studies addressing the mechanistic complexity of catalytic processes by molecular catalysts based on 3d metals. Cases that involve noninnocent ligands, multicomponent reaction systems, metal–ligand and metal–metal cooperativity, as well as modeling complex catalytic systems such as metal–organic frameworks are presented. Conventionally, computational studies on catalytic mechanisms are heavily dependent on the chemical intuition and expert input of the researcher. Recent developments in advanced automated methods for reaction path analysis hold promise for eliminating such human-bias from computational catalysis studies. A brief overview of these approaches is presented in the final section of the review. The paper is closed with general concluding remarks.

